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Winksele, December 23, 2005

Re: International patent application PCT/BE2005/000030

Filing date: 25 February 2005

Applicant: Universiteit Gent

Title: "Metal complexes for use in olefin metathesis and atom group transfer reactions"

Our ref: R3214-PCT/wb/td/aj

To the Written Opinion of the International Searching Authority under PCT Rule 43bis.1, dated 16 September 2005.

Dear Mr. Elliot,

Please find enclosed the Demand form PCT/IPEA/401.

We herewith submit without prejudice a new set of claims 1-57 replacing the claims currently on file.

I. Amended claims and specification

Originally filed claims 1 and 15 (now claims 1 and 14) have been amended to comply with the requirements set out in Re item V Novelty / Inventive Step.

Originally filed claims 5 and 16 have been deleted, with corresponding re-numbering of further claims so as to take into account the changes made to claim 1.

Originally filed claims 24-27 (now claims 22-25) have been amended so as to take into account the changes made to claim 15 (now claim 14).

Originally filed claims 28-29 have been provisionally deleted to comply with the requirements set out in Re item IV.

Originally filed claim 42 (now claim 38) has been amended to comply with the requirements set out in Re item VIII.

The remaining claims have not been changed except for their renumbering or dependency.

A version of the claims with indication of the changes has been added for your information.

Page 7 of the originally filed application has been amended and a new page 7 bis has been created so as to briefly introduce a prior art document.

II. Claim amendments

Originally filed claim 1 has been amended by inserting therein the feature of originally filed claim 5.

Because the amended claim 1 now incorporates the feature of originally filed claim 5, claim 5 has been deleted.

Originally filed claim 15 (now claim 14) has been amended by inserting therein the feature of originally filed claim 16.

A basis for new claim 14 can be found in the originally filed description page 8, lines 19-24 where it is described that *"In particular, this invention is based on the unexpected finding that new and useful catalytic species can be suitably obtained by reacting an acid with a multi-coordinated metal complex, preferably an at least tetra-coordinated transition metal complex, comprising multidentate Schiff base ligand and further comprising a set of other ligands, wherein said set of other ligands is free from any phosphine ligands."* (emphasis added).

Because the amended claim 15 (now claim 14) now incorporates the feature of originally filed claims 16 and 24-27 (now claims 22-25), claim 16 has been deleted and said feature has been deleted from originally filed claims 24-27 (now claims 22-25).

Originally filed claims 28 and 29 have been deleted.

III. Novelty/Inventive Step

WO 99/22865 A (D1) discloses enhancing the catalytic activity of a ruthenium carbene complex by the deliberate addition of specific amounts of organic or inorganic acid, the said enhancement being for a variety of olefin metathesis reactions. One of the catalysts described in **D1** is a Schiff-base-substituted complexes including an alkylidene ligand and a phosphine ligand. It further alleges (page 26, lines 15-17) that the effect of the acid in the system appears to be twofold: in addition to eliminating hydroxide ions which would cause catalyst decomposition, catalyst activity is also enhanced by protonation of phosphine ligands. Because its alleged mechanism of acid activation involves the protonation of phosphine ligands, it is limited to

alkylidene ruthenium complexes including at least one phosphine ligand. It does not disclose reacting a Schiff-base-substituted ruthenium complex devoid of any phosphine ligand with an acid under conditions such that said acid at least partly cleaves a bond between the metal and the Schiff base ligand of said ruthenium complex.

Clercq B. D. et al, Applied catalysis A: General, vol. 247, n° 2, 2003, p.345-364 (D2) discloses a scheme (Scheme 3), wherein a penta-coordinated metal complex anchored to a support comprises one phosphine ligand and one bidentate Schiff base ligand. Said Schiff base ligand comprises an imino group and is coordinated to the metal, in addition to the nitrogen atom of said imino group, through an oxygen atom. Said penta-coordinated metal complex is contacted with an acid and a bond between the metal and the nitrogen atom of said imino group is cleaved as a result of said contact.

None of the cited prior art documents discloses modifying a multicoordinated metal complex free from phosphine ligands. Accordingly, the subject matter of new claims 1 and 14 is novel over both D1 and D2.

Since D1 involves the use of phosphine ligand containing complexes and since the mechanism of enhancing the catalytic activity of said phosphine containing complexes is described as involving the protonation of phosphine ligands, nothing in D1 hints toward the used of acid to enhance the catalytic activity of phosphine-free complexes. Quite at the contrary, the skilled person would be discouraged to use acid together with phosphine-free metal complexes by the disclosure made in D1 that phosphine ligands play an important role in the acid mediated catalysis activity enhancement.

In D2, the only catalyst appearing in scheme 3 comprises a phosphine ligand and there is no hints from D1 that this phosphine ligand could be replaced by something else.

Accordingly, the subject matter of new claims 1 and 14 is inventive over D1 in view of D2.

In virtue of their dependency from new claim 1, new claims 2 to 13 are also novel and inventive over the combination of D1 and D2.

In virtue of their dependency from new claim 14, new claims 15 to 57 are also novel and inventive over the cited prior art. In particular, nothing in the prior art teaches or suggests multicoordinated metallic complexes having any of the structural formulae shown in new claims 22-25.

IV. Lack of unity

To restore unity, originally filed claims 28 and 29 have been provisionally deleted.

We therefore await issuance of a favourable International Preliminary Examination Report. Should this not be the case, we respectfully request issuance of a second Written Opinion. Thank you.

Very truly yours,

A handwritten signature in cursive script that reads "William E Bird".

William E Bird

- Encl.: - Amended claims 1-57, showing amendments (17 pages)
- Amended claims 1-57, clean copy (16 pages)
- New page 7 (1 page)
- New page 7 bis (1 page)
- Demand (5 pages)

1. A method of modifying a multi-coordinated metal, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further
5 heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, ~~characterized in that the said method comprises~~ bringing said multi-coordinated metal complex into contact with an acid under conditions such that said acid is able to at least partly cleave a bond between the metal and said at least one multidentate Schiff base ligand (i), and wherein said other ligands (ii) are
10 selected such as to be unable of protonation by said acid under said conditions, and are not selected from the group consisting of phosphines, amines, arsines and stibines.

2. A method according to claim 1, characterized in that said conditions include a molar ratio between said acid and said multi-coordinated metal complex being above 1.2 and
15 below 40.

3. A method according to claim 1 or claim 2, characterized in that said conditions include a contact time from 5 seconds to 100 hours.

20 4. A method according to any of claims 1 to 3, characterized in that said conditions include a contact temperature from about -50°C to about $+80^{\circ}\text{C}$.

~~5. A method according to any of claims 1 to 4, characterized in that said other ligands (ii) are not selected from the group consisting of phosphines, amines, arsines and
25 stibines.~~

~~65. A method according to any of claims 1 to 54, wherein the pKa of said acid is lower than the pKa of said multidentate Schiff base ligand (ii).~~

30 ~~76. A method according to any of claims 1 to 65, characterized in that at least one of said other ligands (ii) is a constraint steric hindrance ligand having a pKa of at least 15.~~

~~87. A method according to any of claims 1 to 76, characterized in that the number of carbon atoms in said at least one multidentate Schiff base ligand (i), between the~~

nitrogen atom of said imino group and said coordinating heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.

98. A method according to any of claims 1 to 87, characterized in that at least one of said other ligands (ii) is a carbene ligand selected from the group consisting of N-heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

109. A method according to any of claims 1 to 87, characterized in that at least one of said other ligands (ii) is an anionic ligand.

110. A method according to any of claims 1 to 87, characterized in that at least one of said other ligands (ii) is a non-anionic ligand.

121. A method according to any of claims 1 to 110, characterized in that said acid is chlorhydric acid or bromhydric acid.

132. A method according to any of claims 1 to 121, characterized in that said conditions are able to protonate the multidentate Schiff base ligand and decoordinate the nitrogen atom of the imino group of said multidentate Schiff base ligand from the metal.

143. A method according to any of claims 1 to 132, characterized in that said conditions are able to decoordinate the further heteroatom of said multidentate Schiff base ligand from the metal.

154. The reaction product of:

- (a) a multi-coordinated metal complex, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, and
- (b) an acid reacted in a molar ratio above about 1.2 with respect to said multi-coordinated metal complex (a),

provided that said other ligands (ii) are unable of protonation by said acid and are not selected from the group consisting of amines, phosphines, arsines and stibines-

~~16. A product according to claim 15, characterized in that said other ligands (ii) are not selected from the group consisting of amines, phosphines, arsines and stibines.~~

~~17~~15. A product according to claim ~~15-14~~ or claim 16, characterized in that the pKa of said acid (b) is lower than the pKa of said at least one multidentate Schiff base ligand (i).

~~18~~16. A product according to any of claims ~~15-14~~ to 1715, characterized in that the number of carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of said imino group and said heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.

~~19~~17. A product according to any of claims ~~15-14~~ to 1816, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a constraint steric hindrance ligand having a pKa of at least 15.

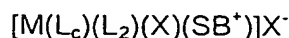
~~20~~18. A product according to any of claims ~~15-14~~ to 1917, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand selected from the group consisting of N-heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

~~21~~19. A product according to any of claims ~~15-14~~ to 2018, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand.

~~22~~20. A product according to any of claims ~~15-14~~ to 2119, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand.

~~23~~21. A product according to any of claims ~~15-14~~ to 2220, characterized in that said acid is chlorhydric acid or bromhydric acid.

2422. A product according to any of claims 45-14 to 2321, being a monometallic species represented by the general formula:

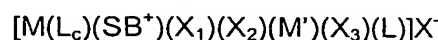


wherein

- 5 - M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- 10 - SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;
- L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- L_2 is a non-anionic ligand, ~~preferably other than a phosphine ligand;~~
- 15 - X is an anionic ligand; and
- X^- is an anion,

salts, solvates and enantiomers thereof.

2523. A product according to any of claims 45-14 to 2321, being a bimetallic species represented by the general formula:

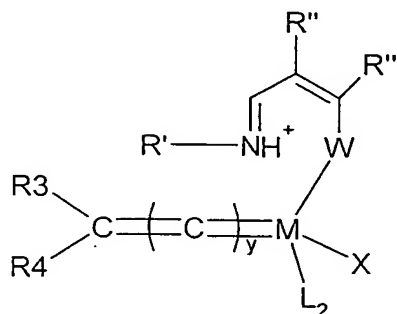


wherein

- 25 - M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;
- 30 - L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- L is a non-anionic ligand, ~~preferably other than a phosphine ligand;~~
- X_1 , X_2 and X_3 are each independently selected from anionic ligands; and
- 35 - X^- is an anion,

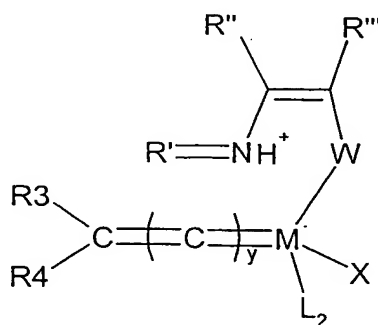
salts, solvates and enantiomers thereof.

2624. A product according to any of claims 15—14 to 2321, being a cationic monometallic species being represented by the general formula (VI):



5

or a cationic monometallic species being represented by the general formula (VII):



wherein

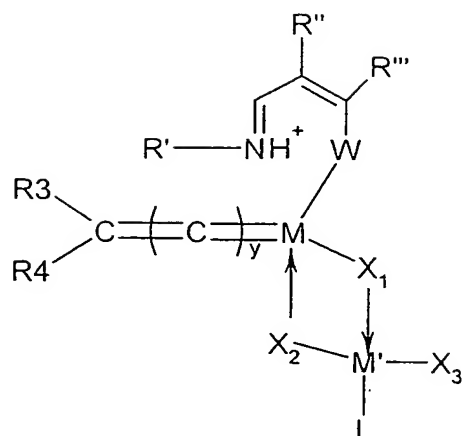
- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''', PR''', AsR''' and SbR''';
- R'', R''' and R'''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate,

alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, alkylammonium and arylammonium;

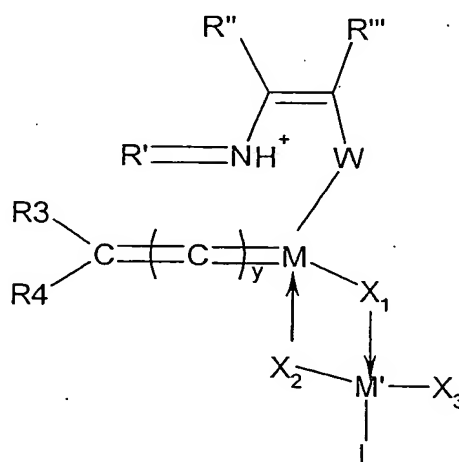
- 5 - R' is either as defined for R'', R''' and R'''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;
- L₂ is a non-anionic ligand, ~~preferably other than a phosphine ligand;~~
- 10 - X is an anionic ligand;
- R₃ and R₄ are each hydrogen or a radical selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium;
- 15 - R' and one of R₃ and R₄ may be bonded to each other to form a bidentate ligand;
- R''' and R'''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
- 20 - R₃ and R₄ together may form a fused aromatic ring system, and
- y represents the number of sp₂ carbon atoms between M and the carbon atom bearing R₃ and R₄ and is an integer from 0 to 3 inclusive,

salts, solvates and enantiomers thereof, and said cationic species being associated with an anion.

2725. A product according to any of claims 45-14 to 2321, being a cationic bimetallic species being represented by the general formula (X):



or a cationic bimetallic species being represented by the general formula (XI):



wherein

- M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''', PR''', AsR''' and SbR''';
- R'', R''' and R'''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3,

substituents R_5 each independently selected from the group consisting of halogen atoms, C_{1-6} alkyl, C_{1-6} alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C_{1-6} alkyl- C_{1-6} alkoxysilyl, C_{1-6} alkyl-aryloxysilyl, C_{1-6} alkyl- C_{3-10} cycloalkoxysilyl, alkylammonium and arylammonium;

5

- R' is either as defined for R'' , R''' and R'''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C_{1-6} alkylene and C_{3-8} cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R_5 ;

10

- R_3 and R_4 are each hydrogen or a radical selected from the group consisting of C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryl, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-8} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl, C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium and arylammonium;

15

- R' and one of R_3 and R_4 may be bonded to each other to form a bidentate ligand;
- R''' and R'''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;

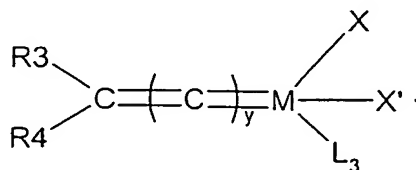
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- R_3 and R_4 together may form a fused aromatic ring system, and
- y represents the number of sp_2 carbon atoms between M and the carbon atom bearing R_3 and R_4 and is an integer from 0 to 3 inclusive,
- X_1 , X_2 and X_3 are each independently selected from anionic ligands; and

25

- L is a non-anionic ligand, preferably other than a phosphine ligand, including salts, solvates and enantiomers thereof.

~~28. A product according to any of claims 15 to 23, being a monometallic complex represented by the general formula (VIII):~~



30 wherein

~~M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;~~

~~X is an anionic ligand;~~

~~R₃ and R₄ are each hydrogen or a radical selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl, C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium;~~

~~R₃ and R₄ together may form a fused aromatic ring system;~~

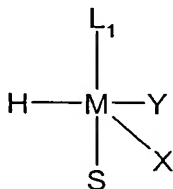
~~y represents the number of sp₂ carbon atoms between M and the carbon atom bearing R₃ and R₄ and is an integer from 0 to 3 inclusive;~~

~~X' is an anionic ligand; and~~

~~L₃ is a non-anionic ligand, other than a phosphine ligand,~~

~~salts, solvates and enantiomers thereof.~~

29. A product according to any of claims 15 to 23, being a monometallic complex represented by the general formula (IX):



wherein:

~~M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;~~

~~X is an anionic ligand;~~

~~S is a solvent;~~

~~Y is a solvent or Y is CO when S is an alcohol; and~~

~~L₁ is a non-anionic ligand, preferably other than a phosphine ligand,~~

~~salts, solvates and enantiomers thereof.~~

3426. A product according to any of claims 45-14 to 2321, at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a solvent S and said complex (a) is a cationic species associated with an anion A.

5 3427. A product according to any of claims 45-14 to 2321, characterized in that said multi-coordinated metal complex (a) is a bimetallic complex.

3428. A product according to claim 3427, characterized in that one metal of said bimetallic complex is penta-coordinated with said at least one multidentate Schiff base ligand (i) and with said one or more other ligands (ii), and the other metal is tetra-coordinated with one or more neutral ligands and one or more anionic ligands.

3429. A product according to claim 3427, characterized in that each metal of said bimetallic complex is hexa-coordinated with said at least one multidentate Schiff base ligand (i) and with said one or more other ligands (ii).

3430. A product according to claim 3427, characterized in that the two metals of the bimetallic complex are the same.

20 3431. A product according to claim 3427, characterized in that the two metals of the bimetallic complex are different.

3432. A product according to any of claims 45-14 to 2321, characterized in that said multi-coordinated metal complex (a) is a monometallic complex.

25 3433. A product according to any of claims 45-14 to 2321, characterized in that the metal of said multi-coordinated metal complex (a) is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table.

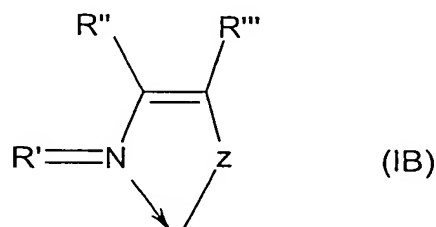
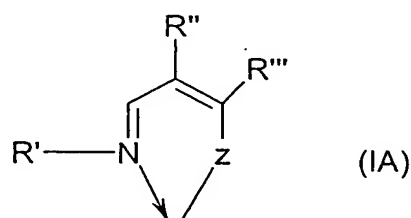
30 3434. A product according to any of claims 45-14 to 2321, characterized in that said metal is selected from the group consisting of ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

3935. A product according to any of claims 45-14 to 2321, characterized in that said multi-coordinated metal complex (a) is a penta-coordinated metal complex or a tetra-coordinated metal complex.

5 4036. A product according to claim 3935, characterized in that said at least one multidentate Schiff base ligand (i) is a bidentate ligand and said multi-coordinated metal complex (a) comprises two other ligands (ii).

10 4137. A product according to claim 3935, characterized in that said at least one multidentate Schiff base ligand (i) is a tridentate ligand and said multi-coordinated metal complex (a) comprises a single other ligand (iii).

15 4238. A product according to claim 39-35 or claim 4036, characterized in that said at least one multidentate Schiff base ligand (i) has one of the general formulae (IA) and (IB); referred to in figure 1, wherein:



wherein:

- Z is selected from the group consisting of oxygen, sulfur and selenium;
- R'' and R''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, alkylammonium and arylammonium;
- R' is either as defined for R'' and R''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₇ alkylene and C₃₋₁₀

cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R_5 .

4339. A product according to claim 3935, characterized in that at least one of said
 5 other ligands (ii) of said multi-coordinated metal complex (a) is a derivative, wherein
 one or more hydrogen atoms is substituted with a group providing constraint steric
 hindrance, of a N-heterocyclic carbene selected from the group consisting of imidazol-
 2-ylidene, dihydroimidazol-2-ylidene, oxazol-2-ylidene, triazol-5-ylidene, thiazol-2-
 ylidene, bis(imidazol-2-ylidene), bis(imidazolidin-2-ylidene), pyrrolylidene,
 10 pyrazolylidene, dihydro-pyrrolylidene, pyrrolylidinylidene and benzo-fused derivatives
 thereof, or a non-ionic phosphatane superbase.

4440. A product according to claim 3935, characterized in that at least one of said
 other ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand
 15 selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkenyl, C_{1-20} alkynyl, C_{1-20}
 carboxylate, C_{1-20} alkoxy, C_{1-20} alkenyloxy, C_{1-20} alkynyloxy, aryl, aryloxy, C_{1-20}
 alkoxycarbonyl, C_{1-8} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl C_{1-20} alkylsulfonate,
 arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium,
 arylammonium, halogen atoms and cyano.

4541. A product according to claim 3935, characterized in that at least one of said
 other ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand
 represented by the general formula $[C=]_yCR_3R_4$, wherein:

- y is an integer from 0 to 3 inclusive, and
- 25 - R_3 and R_4 are each hydrogen or a hydrocarbon radical selected from the group
 consisting of C_{1-20} alkyl, C_{1-20} alkenyl, C_{1-20} alkynyl, C_{1-20} carboxylate, C_{1-20}
 alkoxy, C_{1-20} alkenyloxy, C_{1-20} alkynyloxy, aryl, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-8}
 alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl C_{1-20} alkylsulfonate, arylsulfonate,
 30 C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium and
 arylammonium; or R_3 and R_4 together may form a fused aromatic ring system.

4642. A product according to claim 4541, characterized in that R_3 and R_4 together form
 a fused aromatic ring system such that said other ligand (ii) of said multi-coordinated
 metal complex (a) is a phenylindenylidene ligand.

47.43. A product according to claim 3935, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic unsaturated ligand L¹ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

48.44. A product according to claim 3935, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand L² selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, arylalkyl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

49.45. A product according to claim 3935, characterized in that said at least one multidentate Schiff base ligand (i) is a tetradentate ligand and said multi-coordinated metal complex (a) comprises one or two other ligands (ii) being non-anionic ligands L⁷ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, wherein the said aromatic or unsaturated cycloaliphatic group is optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

50.46. A product according to claim 4514, wherein said acid (b) is an acid generated *in situ* from a photoacid generator.

51.47. A product according to claim 4514, comprising the product of at least partial cleavage of a bond between the metal and said at least one multidentate Schiff base ligand (i).

52-48. A catalytic system comprising:

- (a) as the main catalytic species, a reaction product according to any of claims 45-14 to 5147, and
- (b) one or more second catalyst components being selected from the group consisting of Lewis acid co-catalysts (b_1), catalyst activators (b_2), and initiators having a radically transferable atom or group (b_3).

53-49. A catalytic system according to claim 5248, wherein the second catalyst component includes a co-catalyst (b_1) selected from the group consisting of boron trihalides; phosphorus trihalides; trialkylboron compounds; triarylboron compounds; organoaluminum compounds; magnesium dihalides; aluminum trihalides; tin tetrachloride; titanium or vanadium trihalides or tetrahalides or tetraalkoxides; antimony and bismuth pentahalides.

54-50. A catalytic system according to claim 5248, wherein the second catalyst component includes, as a catalyst activator (b_2), a diazo compound.

55-51. A catalytic system according to claim 5248, wherein the second catalyst component includes, as an initiator having a radically transferable atom or group (b_3), a compound having the formula $R_{35}R_{36}R_{37}CX_1$, wherein:

- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-7} alkyl groups and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$, $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
- R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene group of 2 to 5 carbon

atoms), COCl, OH, CN, C₂₋₂₀ alkenyl (preferably vinyl), C₂₋₂₀ alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C₂₋₂₀ alkenyl.

5652. A supported catalyst, comprising:

- 5 (a) a catalytically active reaction product according to any of claims ~~45-14~~ to ~~51-47~~, or a catalytic system according to claim ~~52-48~~, and
- (b) a supporting amount of a carrier suitable for supporting said catalytically active product or catalytic system (a).

10 5753. A method of performing an olefin or acetylene metathesis reaction or a reaction involving the transfer of an atom or group to an ethylenically or acetylenically unsaturated compound or another reactive substrate in the presence of a catalytic component, wherein the said catalytic component comprises a product according to any of claims ~~45-14~~ to ~~51-47~~ or a catalytic system according to any of claims ~~52-48~~ to
15 5551.

58-54. A method according to claim 5753, wherein said reaction involving the transfer of an atom or group to an olefin or another reactive substrate is selected from the group consisting of:

- 20 - atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
- atom transfer radical addition of a polyhalomethane having the formula CX_nH_{4-n}, wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically
25 unsaturated compound to produce the corresponding saturated polyhalogenated adduct;
- vinylation reaction of a mono- or di-alkyne with a mono- or di-carboxylic acid to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti-Markovnikov adducts or mixtures thereof;
- 30 - cyclopropanation of an α -ethylenically unsaturated compound for producing an organic compound having one or more cyclopropane structural units;
- quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;
- epoxidation of α -ethylenically unsaturated compounds for producing epoxides;

- oxidation of organic compounds including the oxidation of saturated hydrocarbons for producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for producing carboxylic acids;
- 5 - cyclopropanation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
- hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for producing β -cyano carbonyl compounds;
- 10 - hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;
- aziridination of imines or alkenes for producing organic compounds having one or more aziridine structural units;
- 15 - hydroamidation of olefins for producing saturated amides;
- hydrogenation of olefins for producing alkanes, or ketones for producing alcohols;
- aminolysis of olefins for producing saturated primary or secondary amines;
- 20 - isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;
- Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
- hydroboration of olefins for producing alkylboranes and trialkylboranes;
- hydride reduction of aldehydes and ketones for producing alcohols;
- 25 - aldol condensation of saturated carboxyl compounds for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intramolecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds;
- Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
- 30 - Robinson annulation for producing saturated polycyclic carboxyl compounds;
- Heck reactions of an aryl halide or a 1-hetero-2,4-cyclopentadiene or a benzo-fused derivative thereof with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
- 35

- codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
- hydroxylation of olefins for producing alcohols;
- hydroamination of olefins and alkynes for producing amines;
- 5 - alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones; and
- Diels-Alder reactions such as the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated
10 compound for producing optionally substituted 7-oxanorbornenes.

59-55. A method according to claim 5753, wherein the said metathesis reaction is the ring-opening metathesis polymerisation of strained cyclic olefins.

- 15 60-56. A method according to claim 5753, wherein the catalytic component is supported on a carrier.

- 61-57. A method according to claim 6056, wherein the said carrier is selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline
20 materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins.

1. A method of modifying a multi-coordinated metal, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further
5 heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, said method comprising bringing said multi-coordinated metal complex into contact with an acid under conditions such that said acid is able to at least partly cleave a bond between the metal and said at least one multidentate Schiff base ligand (i), and wherein said other ligands (ii) are selected such as to be
10 unable of protonation by said acid under said conditions, and are not selected from the group consisting of phosphines, amines, arsines and stibines
2. A method according to claim 1, characterized in that said conditions include a molar ratio between said acid and said multi-coordinated metal complex being above 1.2 and
15 below 40.
3. A method according to claim 1 or claim 2, characterized in that said conditions include a contact time from 5 seconds to 100 hours.
- 20 4. A method according to any of claims 1 to 3, characterized in that said conditions include a contact temperature from about -50°C to about $+80^{\circ}\text{C}$.
5. A method according to any of claims 1 to 4, wherein the pK_a of said acid is lower than the pK_a of said multidentate Schiff base ligand (ii).
25
6. A method according to any of claims 1 to 5, characterized in that at least one of said other ligands (ii) is a constraint steric hindrance ligand having a pK_a of at least 15.
7. A method according to any of claims 1 to 6, characterized in that the number of
30 carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of said imino group and said coordinating heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.
8. A method according to any of claims 1 to 7, characterized in that at least one of said
35 other ligands (ii) is a carbene ligand selected from the group consisting of N-

heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

9. A method according to any of claims 1 to 7, characterized in that at least one of said
5 other ligands (ii) is an anionic ligand.

10. A method according to any of claims 1 to 7, characterized in that at least one of said other ligands (ii) is a non-anionic ligand.

10 11. A method according to any of claims 1 to 10, characterized in that said acid is chlorhydric acid or bromhydric acid.

12. A method according to any of claims 1 to 11, characterized in that said conditions are able to protonate the multidentate Schiff base ligand and decoordinate the nitrogen
15 atom of the imino group of said multidentate Schiff base ligand from the metal.

13. A method according to any of claims 1 to 12, characterized in that said conditions are able to decoordinate the further heteroatom of said multidentate Schiff base ligand from the metal.

20

14. The reaction product of:

(a) a multi-coordinated metal complex, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the
25 nitrogen atom of said imino group, through at least one further heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, and

(b) an acid reacted in a molar ratio above about 1.2 with respect to said multi-coordinated metal complex (a),

30 provided that said other ligands (ii) are unable of protonation by said acid and are not selected from the group consisting of amines, phosphines, arsines and stibines

15. A product according to claim 14, characterized in that the pKa of said acid (b) is
35 lower than the pKa of said at least one multidentate Schiff base ligand (i).

16. A product according to any of claims 14 to 15, characterized in that the number of carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of said imino group and said heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.

17. A product according to any of claims 14 to 16, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a constraint steric hindrance ligand having a pKa of at least 15.

10

18. A product according to any of claims 14 to 17, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand selected from the group consisting of N-heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

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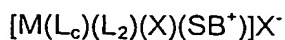
19. A product according to any of claims 14 to 17, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand.

20. A product according to any of claims 14 to 17, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand.

21. A product according to any of claims 14 to 20, characterized in that said acid is chlorhydric acid or bromhydric acid.

25

22. A product according to any of claims 14 to 21, being a monometallic species represented by the general formula:



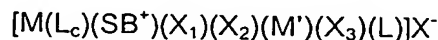
wherein

- 30 - M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- SB⁺ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;

35

- L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
 - L_2 is a non-anionic ligand;
 - 5 - X is an anionic ligand; and
 - X^- is an anion,
- salts, solvates and enantiomers thereof.

23. A product according to any of claims 14 to 21, being a bimetallic species represented by the general formula:

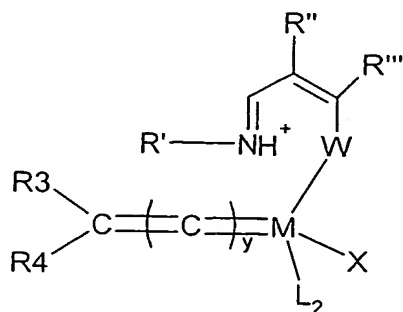


wherein

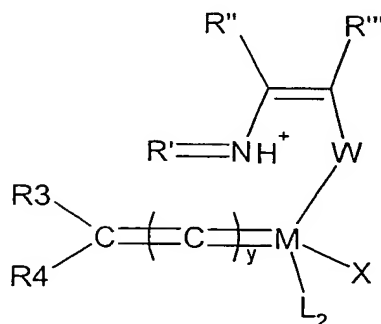
- M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;
- 20 - L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- L is a non-anionic ligand;
- X_1 , X_2 and X_3 are each independently selected from anionic ligands; and
- 25 - X^- is an anion,

salts, solvates and enantiomers thereof.

24. A product according to any of claims 14 to 21, being a cationic monometallic species being represented by the general formula (VI):



or a cationic monometallic species being represented by the general formula (VII):

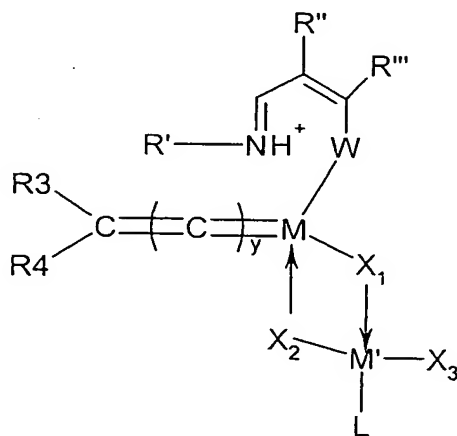


wherein

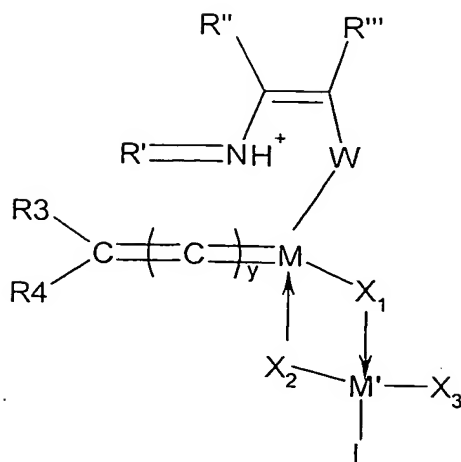
- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''', PR''', AsR''' and SbR''';
- R'', R''' and R'''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, alkylammonium and arylammonium;
- R' is either as defined for R'', R''' and R'''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;
- L₂ is a non-anionic ligand;
- X is an anionic ligand;

- R_3 and R_4 are each hydrogen or a radical selected from the group consisting of C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryl, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-8} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl, C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium and arylammonium;
 - R' and one of R_3 and R_4 may be bonded to each other to form a bidentate ligand;
 - R'' and R''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
 - R_3 and R_4 together may form a fused aromatic ring system, and
 - y represents the number of sp_2 carbon atoms between M and the carbon atom bearing R_3 and R_4 and is an integer from 0 to 3 inclusive,
- salts, solvates and enantiomers thereof, and said cationic species being associated with an anion.

25. A product according to any of claims 14 to 21, being a cationic bimetallic species being represented by the general formula (X):



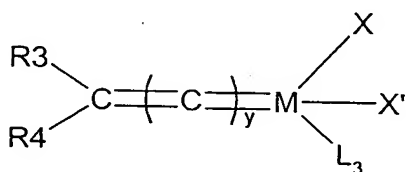
or a cationic bimetallic species being represented by the general formula (XI):



wherein

- M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''', PR''', AsR''' and SbR''';
- R'', R''' and R'''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxyethyl, C₁₋₆ alkyl-aryloxyethyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxyethyl, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxyethyl, C₁₋₆ alkyl-aryloxyethyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxyethyl, alkylammonium and arylammonium;
- R' is either as defined for R'', R''' and R'''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;

- R_3 and R_4 are each hydrogen or a radical selected from the group consisting of C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryl, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-8} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl, C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium and arylammonium;
 - R' and one of R_3 and R_4 may be bonded to each other to form a bidentate ligand;
 - R''' and R'''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
 - R_3 and R_4 together may form a fused aromatic ring system, and
 - y represents the number of sp_2 carbon atoms between M and the carbon atom bearing R_3 and R_4 and is an integer from 0 to 3 inclusive,
 - X_1 , X_2 and X_3 are each independently selected from anionic ligands; and
 - L is a non-anionic ligand,
- including salts, solvates and enantiomers thereof.



26. A product according to any of claims 14 to 21, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a solvent S and said complex (a) is a cationic species associated with an anion A .

27. A product according to any of claims 14 to 21, characterized in that said multi-coordinated metal complex (a) is a bimetallic complex.

28. A product according to claim 27, characterized in that one metal of said bimetallic complex is penta-coordinated with said at least one multidentate Schiff base ligand (i)

and with said one or more other ligands (ii), and the other metal is tetra-coordinated with one or more neutral ligands and one or more anionic ligands.

5 29. A product according to claim 27, characterized in that each metal of said bimetallic complex is hexa-coordinated with said at least one multidentate Schiff base ligand (i) and with said one or more other ligands (ii).

10 30. A product according to claim 27, characterized in that the two metals of the bimetallic complex are the same.

31. A product according to claim 27, characterized in that the two metals of the bimetallic complex are different.

15 32. A product according to any of claims 14 to 21, characterized in that said multi-coordinated metal complex (a) is a monometallic complex.

20 33. A product according to any of claims 14 to 21, characterized in that the metal of said multi-coordinated metal complex (a) is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table.

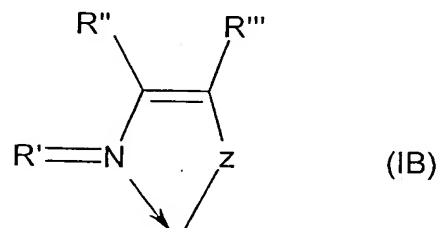
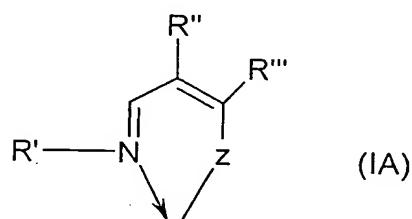
25 34. A product according to any of claims 14 to 21, characterized in that said metal is selected from the group consisting of ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

35. A product according to any of claims 14 to 21, characterized in that said multi-coordinated metal complex (a) is a penta-coordinated metal complex or a tetra-coordinated metal complex.

30 36. A product according to claim 35, characterized in that said at least one multidentate Schiff base ligand (i) is a bidentate ligand and said multi-coordinated metal complex (a) comprises two other ligands (ii).

37. A product according to claim 35, characterized in that said at least one multidentate Schiff base ligand (i) is a tridentate ligand and said multi-coordinated metal complex (a) comprises a single other ligand (iii).

- 5 38. A product according to claim 35 or claim 36, characterized in that said at least one multidentate Schiff base ligand (i) has one of the general formulae (IA) and (IB):



wherein:

- Z is selected from the group consisting of oxygen, sulfur and selenium;
- 10 - R'' and R''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, alkylammonium and arylammonium;
- 15 - R' is either as defined for R'' and R''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₇ alkylene and C₃₋₁₀ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅.
- 20
- 25 39. A product according to claim 35, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a derivative, wherein one or more hydrogen atoms is substituted with a group providing constraint steric hindrance, of a N-heterocyclic carbene selected from the group consisting of imidazol-2-ylidene, dihydroimidazol-2-ylidene, oxazol-2-ylidene, triazol-5-ylidene, thiazol-2-ylidene, bis(imidazol-2-ylidene), bis(imidazolidin-2-ylidene), pyrrolylidene, pyrazolylidene,
- 30

dihydro-pyrrolylidene, pyrrolylidinylidene and benzo-fused derivatives thereof, or a non-ionic prophosphatane superbase.

40. A product according to claim 35, characterized in that at least one of said other
 5 ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkenyl, C₁₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₁₋₂₀ alkenyloxy, C₁₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxy carbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium, arylammonium, halogen
 10 atoms and cyano.

41. A product according to claim 35, characterized in that at least one of said other
 ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand represented
 by the general formula $=[C=]_yCR_3R_4$, wherein:

- 15 - y is an integer from 0 to 3 inclusive, and
- R₃ and R₄ are each hydrogen or a hydrocarbon radical selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkenyl, C₁₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₁₋₂₀ alkenyloxy, C₁₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxy carbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate,
 20 C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium; or R₃ and R₄ together may form a fused aromatic ring system.

42. A product according to claim 41, characterized in that R₃ and R₄ together form a
 fused aromatic ring system such that said other ligand (ii) of said multi-coordinated
 25 metal complex (a) is a phenylindenylidene ligand.

43. A product according to claim 35, characterized in that at least one of said other
 ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic unsaturated
 ligand L¹ selected from the group consisting of aromatic and unsaturated cycloaliphatic
 30 groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

44. A product according to claim 35, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand L^2 selected from the group consisting of C_{1-7} alkyl, C_{3-10} cycloalkyl, arylalkyl and heterocyclic, the said group being optionally substituted with one or more preferably
 5 electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
45. A product according to claim 35, characterized in that said at least one multidentate
 10 Schiff base ligand (i) is a tetradentate ligand and said multi-coordinated metal complex (a) comprises one or two other ligands (ii) being non-anionic ligands L^7 selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C_{4-20} cycloalkenyl groups, wherein the said aromatic or unsaturated cycloaliphatic group is optionally substituted with one or more C_{1-7} alkyl groups or
 15 electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
46. A product according to claim 14, wherein said acid (b) is an acid generated *in situ*
 20 from a photoacid generator.
47. A product according to claim 14, comprising the product of at least partial cleavage
 of a bond between the metal and said at least one multidentate Schiff base ligand (i).
 25
48. A catalytic system comprising:
 (a) as the main catalytic species, a reaction product according to any of
 claims 14 to 47, and
 (b) one or more second catalyst components being selected from the group
 30 consisting of Lewis acid co-catalysts (b_1), catalyst activators (b_2), and initiators having a radically transferable atom or group (b_3).
49. A catalytic system according to claim 48, wherein the second catalyst component
 includes a co-catalyst (b_1) selected from the group consisting of boron trihalides;
 35 phosphorus trihalides; trialkylboron compounds; triarylboron compounds;

organoaluminum compounds; magnesium dihalides; aluminum trihalides; tin tetrachloride; titanium or vanadium trihalides or tetrahalides or tetraalkoxides; antimony and bismuth pentahalides.

5 50. A catalytic system according to claim 48, wherein the second catalyst component includes, as a catalyst activator (b_2), a diazo compound.

51. A catalytic system according to claim 48, wherein the second catalyst component includes, as an initiator having a radically transferable atom or group (b_3), a
10 compound having the formula $R_{35}R_{36}R_{37}CX_1$, wherein:

- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-7} alkyl groups and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$,
15 $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
- R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of
20 hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene group of 2 to 5 carbon
25 atoms), $COCl$, OH , CN , C_{2-20} alkenyl (preferably vinyl), C_{2-20} alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C_{2-20} alkenyl.

52. A supported catalyst, comprising:

- (a) a catalytically active reaction product according to any of claims 14 to
30 47, or a catalytic system according to claim 48, and
- (b) a supporting amount of a carrier suitable for supporting said catalytically active product or catalytic system (a).

53. A method of performing an olefin or acetylene metathesis reaction or a reaction
35 involving the transfer of an atom or group to an ethylenically or acetylenically

unsaturated compound or another reactive substrate in the presence of a catalytic component, wherein the said catalytic component comprises a product according to any of claims 14 to 47 or a catalytic system according to any of claims 48 to 51.

5 54. A method according to claim 53, wherein said reaction involving the transfer of an atom or group to an olefin or another reactive substrate is selected from the group consisting of:

- 10 - atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
- atom transfer radical addition of a polyhalomethane having the formula CX_nH_{4-n} , wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically unsaturated compound to produce the corresponding saturated polyhalogenated adduct;
- 15 - vinylation reaction of a mono- or di-alkyne with a mono- or di-carboxylic acid to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti-Markovnikov adducts or mixtures thereof;
- cyclopropanation of an α -ethylenically unsaturated compound for producing an organic compound having one or more cyclopropane structural units;
- 20 - quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;
- epoxidation of α -ethylenically unsaturated compounds for producing epoxides;
- oxidation of organic compounds including the oxidation of saturated hydrocarbons for producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for producing carboxylic acids;
- 25 - cyclopropenation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
- hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for producing β -cyano carbonyl compounds;
- 30 - hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;
- 35

- aziridination of imines or alkenes for producing organic compounds having one or more aziridine structural units;
 - hydroamidation of olefins for producing saturated amides;
 - hydrogenation of olefins for producing alkanes, or ketones for producing alcohols;
 - aminolysis of olefins for producing saturated primary or secondary amines;
 - isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;
 - Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
 - hydroboration of olefins for producing alkylboranes and trialkylboranes;
 - hydride reduction of aldehydes and ketones for producing alcohols;
 - aldol condensation of saturated carboxyl compounds for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intramolecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds;
 - Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
 - Robinson annulation for producing saturated polycyclic carboxyl compounds;
 - Heck reactions of an aryl halide or a 1-hetero-2,4-cyclopentadiene or a benzo-fused derivative thereof with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
 - codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
 - hydroxylation of olefins for producing alcohols;
 - hydroamination of olefins and alkynes for producing amines;
 - alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones; and
 - Diels-Alder reactions such as the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for producing optionally substituted 7-oxanorbornenes.
55. A method according to claim 53, wherein the said metathesis reaction is the ring-opening metathesis polymerisation of strained cyclic olefins.

56. A method according to claim 53, wherein the catalytic component is supported on a carrier.
- 5 57. A method according to claim 56, wherein the said carrier is selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins.

resonance) and that the effect of the acid in the system appears to be twofold: in addition to eliminating hydroxide ions which would cause catalyst decomposition, catalyst activity is also enhanced by protonation of phosphine ligands. It is also taught that, remarkably, the acids do not react with the ruthenium alkylidene bond.

Although providing an improvement over existing ROMP catalysts, the teaching of U.S. Patent No. 6,284,852 is limited in many aspects, namely:

- because its alleged mechanism of acid activation involves the protonation of phosphine ligands, it is limited to alkylidene ruthenium complexes including at least one phosphine ligand;
- it does not disclose reacting a Schiff-base-substituted ruthenium complex with an acid under conditions such that said acid at least partly cleaves a bond between the metal and the Schiff base ligand of said ruthenium complex.

U.S. Patent No. 6,284,852 does not either teach the behaviour, in the presence of an acid, of ruthenium complexes wherein ruthenium is coordinated with a vinylidene ligand, an allenylidene ligand or a N-heterocyclic carbene ligand.

U.S. Patent No. 6,284,852 therefore has left open ways for the study of metal complexes, in particular multicoordinated ruthenium and osmium complexes in an acidic, preferably a strongly acidic, environment when used for olefin metathesis reactions including ROMP, RCM, ADMET and cross-metathesis and dimerization reactions.

Applied catalysis A (2003) 247:345 discloses the catalytic behavior of Schiff base and phosphine containing ruthenium complexes having been covalently anchored to a solid support. In this document, vinylation experiments are described where a large amount of a carboxylic acid (110 eq/cat) is used as a reactant. This document further postulates a mechanism that explains for observed selectivities in vinylation experiments. In that mechanism, a first step involves a "one arm" dissociation of the bidentate Schiff base ligand, followed by coordination of an allylic carboxylate group. *Applied catalysis A* (2003) 247:345 does not report improvement of the catalytic activity that would be induced by the presence of the acid.

Therefore one goal of this invention is the design of new and useful catalytic species, especially based on multicoordinated transition metal complexes, having unexpected properties and improved efficiency in olefin metathesis reactions as well as in other atom or group transfer reactions such as ATRP or ATRA.

Another goal of this invention is to efficiently perform olefin metathesis reactions, in particular ring opening polymerization of strained cyclic olefins (including cationic forms of such monomers such as, but not limited to, strained cyclic olefins including

quaternary ammonium salts), in the presence of multicoordinated transition metal complexes without being limited by the requirement of a phosphine ligand in said complexes.

There is also a specific need in the art, which is yet another goal of this invention, for improving reaction-injection molding (RIM) processes, resin transfer molding (RTM) processes and reactive rotational molding (RRM) processes such as, but not limited to, the bulk polymerisation of endo- or exo-dicyclopentadiene, or copolymerization thereof with other monomers, or formulations thereof, with the use of multicoordinated transition metal complexes, in particular ruthenium complexes, having various combinations of ligands but which do not necessarily comprise phosphine ligands. All the above needs